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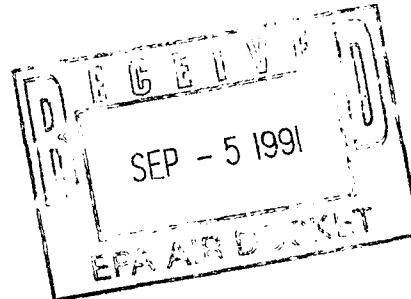
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Environmental and Safety
Engineering Staff
Ford Motor Company

The American Road
Dearborn, Michigan 48121

September 4, 1991

Ms. Mary T. Smith (EN-397)
Director
Field Operations Support Division
U.S. Environmental Protection Agency
401 M Street, S.W.
Washington, DC 20460



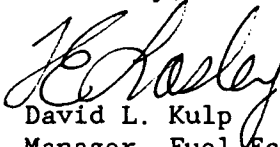
Reference: Air Docket No. A-91-46

Dear Ms. Smith:

As we discussed, Ford has conducted a vehicle test program to evaluate the effect of MMT at a concentration of 1/32 grams/gallon on vehicle emission performance and emission control device and system function. This letter is provided to transmit interim test reports on that program. Commercial-grade fuel was used for mileage accumulation, with MMT being added for designated vehicles.

The eight test vehicles have all completed 105,000 miles durability testing and emission testing, with the exception of one vehicle which needs to test at the 105,000-mile point. The enclosed Ford reports evaluate the effect of MMT on these vehicles through the 55,000-mile test point. Our testing demonstrates a statistically significant increase in HC emissions, a decrease in CO emissions, and an increase in NOx emissions. The data through 105,000 miles show a much greater HC problem, little effect of MMT on CO and a clear increase in NOx emissions. These findings differ substantially from those reported in the waiver application. A summary of the data through 105,000 miles will be provided to you as it becomes available.

Sincerely,

for 
David L. Kulp
Manager, Fuel Economy
Planning & Compliance

Enclosures

cc: Mr. David Kortum
Mr. Don Lynam
Ms. Barbara Little

Particulate Emissions from Current Model Vehicles Using Gasoline with Methylcyclopentadienyl Manganese Tricarbonyl

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ABSTRACT

Particulate and manganese mass emissions have been measured as a function of mileage for four Escort and four Explorer vehicles using both methylcyclopentadienyl manganese tricarbonyl (MMT) gasoline at 1/32 g Mn/gal and MMT-free gasoline. The vehicles were driven on public roads at an average speed of 54 mph to accumulate mileage, and the MMT was used in half of the fleet starting at 5,000 miles. This is an interim report describing the particulate and manganese emissions at 5,000, 20,000 and 55,000 miles. These vehicles are scheduled to continue mileage accumulation to 105,000 miles with emission testing at 85,000 and 105,000 miles. Of the total manganese used in the fuel, between 6% and 45% was emitted as airborne particulate matter, and the remainder was probably stored in the engine, catalyst and the exhaust system. The percentage of the manganese that was emitted increased with mileage accumulation. The EPA reports that manganese emissions of this magnitude may represent a health hazard. Also about 8% of the manganese used in the fuel was found in the engine oil. The manganese that is stored in the engine, catalyst and the exhaust system will be analyzed when the vehicles reach 105,000 miles. The total particulate emissions were between 0 and 5 mg/mi increasing with mileage accumulation and with MMT usage. The regulated emissions are approximately 0.3 g HC/mi, 3 g CO/mi and 0.4 g NO_x/mi. The regulated and non-regulated gaseous emissions will be described in companion reports.

MEASUREMENTS OF REGULATED and so called "non-regulated" emissions are required to show that gasoline additives do not cause emissions that could harm the environment. In general, a fuel additive could cause such damage either directly by forming harmful combustion products or indirectly by damaging vehicle emission control systems.

Methylcyclopentadienyl manganese tricarbonyl (MMT) is an anti-knock gasoline additive whose combustion products are known to accumulate in engines (1)*, on exhaust catalysts (2) and to be released into the atmosphere (3). In each place, they have the potential to harm the environment. In engines, they can cause increased regulated emissions (1), especially of hydrocarbons. On catalysts, they may cause deactivation (2) and, as airborne particulate matter, they can cause neurological effects similar to Parkinson's disease (4).

The magnitudes of these MMT effects depend on the level of MMT added to the gasoline and, perhaps, on the vehicles. In this work, the exhaust emissions from four vehicles, two 1.9L Escorts and two 4.0L Explorers, using MMT fuel at 1/32 g Mn/gal are compared to those from four similar vehicles using MMT-free fuel. These vehicles are equipped with sequential electronic fuel injection and three-way catalyst emission control systems achieving approximately 0.3 g HC/mi, 3 g CO/mi and 0.4 g NO_x/mi. This report, which describes the

* Numbers in parentheses designate references at end of paper.

regulated and particulate emissions from tests at 5K, 20K and 55K miles, was prepared to summarize the work to date; a final report will be prepared when tests planned for 85K and 105K miles are completed.

METHOD

Vehicles Eight vehicles were used in this work, four 4.0L Explorers and four 1.9L Escorts. The Explorers were 1991 production vehicles with 1993 prototype engines equipped with sequential electronic fuel injection systems, automatic transmissions, and two under body three-way catalysts (Pt:Rh, 5:1, 40 g/ft³ precious metal and 75 in³ each). The vehicles had 4500 lb inertia weight and were tested at 13.6 HP load.

The Escorts were 1991 production vehicles with sequential electronic fuel injection, manual transmissions, and one three-way catalyst (Pd:Rh, 9:1, 60 g/ft³ precious metal, and 92 in³ mounted close to the exhaust manifold. The Escorts had 2750 lb inertia and were tested at 7.9 HP. During the testing, both the Escorts and Explorers underwent routine maintenance checks as described in the owner manual.

Fuel All of the vehicles were driven for the first 5,000 miles on MMT-free durability fuel. Then two Escorts, vehicles #316 and #318, and two Explorers, #304 and #306, were changed to the same durability fuel with MMT added at 0.029 g Mn/gal, i.e. 1/32 g Mn/gal, for subsequent mileage accumulation (Appendix Table A1 shows the fuel composition). The other vehicles, #315, #317, #305 and #307, continued to use MMT-free durability fuel.

The durability fuel is Chevron unleaded gasoline with Chevron's patented polyether amine additive in commercially available concentration. This fuel was selected because it contains additives that are normally encountered in customer driving. The composition of the fuel was seasonally adjusted.

Durability Driving These vehicles accumulated mileage on public roads. The route included 5% city driving, 5% gravel roads, 20% rural driving and 70% highway driving. The average speed was 54 mph.

Regulated Emissions The regulated emissions, HC, CO and NO_x, from these vehicles were measured in six repeat tests at 5,000, 20,000 and 55,000 miles (Table I). The

Table I.

Emission Test for the Particulate Matter Measurements

		Odometer (miles)				
<u>Vehicles</u>	<u>MMT Additives</u>	<u>5,000</u>	<u>20,000</u>	<u>55,000</u>	<u>85,000</u>	<u>105,000</u>
Explorers						
#304	Yes	RE	RE	RE,PM	RE	RE,PM
#305	No	RE,PM	RE,PM	RE,PM	RE,PM	RE,PM
#306	Yes	RE,PM	RE,PM	RE,PM	RE,PM	RE,PM
#307	No	RE	RE	RE,PM	RE	RE,PM
Escorts						
#315	No	RE,PM	RE,PM	RE,PM	RE,PM	RE,PM
#316	Yes	RE,PM	RE,PM	RE,PM	RE,PM	RE,PM
#317	No	RE	RE	RE,PM	RE	RE,PM
#318	Yes	RE	RE	RE,PM	RE	RE,PM

RE is regulated emissions and PM is particulate matter measurements.

emissions measurements at 5,000 were done before the introduction of MMT, and those at 20,000 and 55,000 miles were done after MMT was used in some vehicles. Data for vehicle #318 is not reported because it was delayed by a traffic accident. Further tests are planned for

all vehicles at 85,000 and 105,000 miles.

These regulated emission tests were done on a single certification test facility to eliminate "cell-to-cell" variability. In addition, this facility has frequent maintenance and calibration checks, and regular correlation tests with the EPA.

Table II.

Regulated Emissions									
Vehicle Number	Odometer (miles)	Correlation Cell				Particulate Cell			
		HC g/mi	CO g/mi	NO _x g/mi	No of Tests	HC g/mi	CO g/mi	NO _x g/mi	No of Tests
304	55,000	.548 ±.061	3.242 ±.206	.200 ±.009	6	.467 ±.059	3.513 ±.753	.207 ±.007	2
305	5,000	.120 ±.008	1.840 ±.184	.118 ±.015	6	.126	1.898	.139	1
	20,000	.119 ±.003	2.228 ±.146	.141 ±.012	6	.113	1.974	.190	1
	55,000	.154 ±.004	3.596 ±.252	.131 ±.008	6	.152 ±.017	3.383 ±.305	.190 ±.009	3
306	5,000	.142 ±.010	1.812 ±.113	.106 ±.009	6	.147	1.735	.123	1
	20,000	.172 ±.014	2.279 ±.140	.078 ±.010	6	.176	2.775	.153	1
	55,000	.173 ±.016	1.734 ±.125	.314 ±.056	6	.188 ±.023	2.058 ±.227	.334 ±.008	2
307	55,000	.353 ±.034	4.709 ±.377	.178 ±.019	6	.306 ±.028	4.315 ±.325	.156 ±.003	2
315	5,000	.092 ±.011	.832 ±.073	.298 ±.031	6	.113	.741	.190	1
	20,000	.146 ±.030	1.397 ±.421	.327 ±.053	6	.183 ±.006	.937 ±.017	.302 ±.031	2
	55,000	.184 ±.020	1.944 ±.338	.384 ±.034	6	.195 ±.021	1.203 ±.014	.333 ±.025	2
316	5,000	.088 ±.009	.840 ±.154	.249 ±.028	6	.178	1.373	.264	1
	20,000	.161 ±.019	1.488 ±.209	.302 ±.025	6	.211 ±.043	1.326 ±.340	.280 ±.061	2
	55,000	.332 ±.095	2.116 ±.550	.386 ±.047	6	.239 ±.002	1.290 ±.031	.452 ±.039	2
317	55,000	.189 ±.020	1.708 ±.219	.396 ±.035	6	.171 ±.016	1.132 ±.087	.429 ±.023	2
Note: standard deviations are shown; the correlation and particulate cells used EEE and durability fuels, respectively.									

These tests used exhaust and evaporative emissions (EEE) fuel without MMT (Appendix Table A1 shows fuel properties) so as not to contaminate the certification test cell with MMT.

Regulated emissions were also measured during the particulate tests which were done in another cell equipped with a dilution tube. Here the particulate tests were done using durability fuel, either with or without MMT according to the vehicle tested (Table I). The emissions were measured at 5,000 miles, after the introduction of MMT to those vehicles, and again at 20,000 and 55,000 miles. Again further tests are planned at 85,000 and 105,000 miles.

The regulated emissions measured at the two facilities roughly agree within the experimental uncertainty (Table II). The program average emissions from the two facilities agreed within 1%, 7% and 4% for HC, CO and NO_x , respectively, but about 35% of the emission measurements from the two cells are more than two standard deviations apart. While the causes of these differences are not clear, one factor appears to be the fuel changes between tests at the two facilities. Tests with another vehicle showed that regulated emission measurements from the two cells agreed within 10%. An analysis of the effect of MMT on the regulated and non-regulated gaseous emissions will be described in the companion reports.

Particulate Mass Measurements For these analyses, the vehicle exhaust is transferred to a dilution tube through a line which was heated to 235°F. The exhaust is mixed co-currently with dilution air in a 12 inch diameter and 33 foot long stainless steel tube. The dilution air is conditioned and temperature controlled; it, together with the vehicle exhaust, is held at a constant flow rate of 400 scfm and a constant temperature of 85°F. A complete description of the dilution tube was given in a previous report (5).

The particulate measurements are made using filters located approximately 20 feet downstream of the exhaust mixing point on the tube. The filter samples are isokinetically drawn from the tube at four independent, but closely spaced, sites. Two 142 mm diameter filters are used to measure total particulate mass emissions, and two 47 mm diameter filters are used to measure Mn emissions. The flow rates through the 47 and 142 mm filters are about 0.7 and 1.6 scfm, respectively. Even with the 142

mm filters, it is difficult to collect sufficient particulate mass for accurate determination of particulate mass emissions.

To increase the particulate mass collected during these tests, six consecutive, 3-phase cycles are used for these studies. The entire test takes about six hours. The first cycle is a typical 3-phase Urban Dynamometer Driving Schedule (UDDS) test with its usual cold start. The regulated emissions were measured during these 3-phases. After a 10 minute pause with the engine off, it is followed by a second 3-phase cycle, and similarly the third 3-phase cycle. After a 60 minute break, three more 3-phase cycles are conducted. The particulate emissions from all six 3-phase cycles were collected on one filter.

Two different teflon membrane filters from Gelman Sciences were used in most of this work, 0.5 μ pore size Zeflur and 0.2 μ PTFE. In addition, some tests were done using 1.0 μ pore size Zeflur and 0.45 μ pore size PTFE filters for comparison. The filter pore size had no observable effect on the filter trapping efficiency. In addition some tests were done using TX40 HI20WW filters (Teflon-coated glass fiber).

TX40 filters were used at the beginning of the work, but they tended to come apart as they were removed from the filter holders after the test. When the filter was removed from the filter holder, very small pieces of the TX40 filter clung to the "o" ring seal in the holder. These pieces would have to be removed from the "o" ring and added to the filter in order to get accurate weight gain measurements. Since the weight gain due to the particulate matter collected was between 0.1 mg and 1 mg, it was extremely difficult to insure that enough of the stray TX40 was recovered. Therefore, use of the TX40 was discontinued.

The mass of each filter was determined at least six times both before and after particulate collection. Before weighing, the filters were placed in a temperature and humidity controlled room for at least 24 hours. After a filter had reached equilibrium with the room, it was placed on the balance, measured and removed. This process was repeated at least six times. An alpha emitter was placed near the filter to reduce the effects of static charge. An example of the more accurate measurements are shown in Table III. They were done using the Escort #316 at 20,252 and 20,328 miles on site 2.

Mn Particulate Analyses Mn was extracted from the 47 mm filters with 25 ml of 5% HCl in aqueous solution. The filter and HCl solution were placed in a sealed polyethylene vile. The vile was shaken for 16 hours in an automated wrist action shaker. The resulting solution was analyzed for Mn by inductively coupled plasma mass spectrometry. Detection limits were a few

parts per billion by weight. Second extractions of several filters, from which high levels of Mn were initially extracted, had little or no Mn.

Mn Oil Analyses At the regularly scheduled oil changes, a sample of used oil was drained from the vehicles for Mn analysis to help establish Mn material balance. Analyses were done using carbon-arc emission spectroscopy.

Table III.
Masses of the 142 mm PTFE Filters

ID	One 3-Phase Test		Six 3-Phase Tests	
	After (grams)	Before (grams)	After (grams)	Before (grams)
1	0.94869	0.94860	0.94994	0.94927
2	0.94871	0.94857	0.94993	0.94930
3	0.94863	0.94855	0.94999	0.94929
4	0.94873	0.94852	0.94998	0.94932
5	0.94875	0.94857	0.94998	0.94926
6	0.94876	0.94858	0.94997	0.94929
7	<u>0.94871</u>	<u>0.94857</u>	<u>0.94999</u>	<u>0.94930</u>
Ave	0.94871	0.94857	0.94997	0.94929
Std Dev	0.00004	0.00002	0.00002	0.00002
Gain	0.00014	g	0.00068	g
Std Dev	0.000045	g	0.000028	g
% Std Dev	32%		4%	
Dilution	261		283	
Mileage	11.1 mi		66.6 mi	
Particle emission	2.6 mg/mi		1.9 mg/mi	
	± 0.8 mg/mi		± 0.2 mg/mi	

RESULTS

The total particulate mass emissions from these vehicles are generally between 0 and 10 mg/mile (Tables IV and V). The standard deviations due to variability in the weighing measurements are between 0.3 and 2.0 mg/mi (Tables III, IV and V). These weighing errors are approximately the same as the variability in repeat measurements, which is usually about 0.5 mg/mi, but can be as high as 1.6 mg/mi in some cases. For example, the mean and standard

deviations of the 5 separate measurements of the particulate mass emissions for vehicle #305 at 55,000 miles are 2.1 ± 0.5 mg/mi.

Earlier work has shown that there is no significant difference between particulate sampling at sites 1 and 2. While site 1 apparently yields more particulate mass (an average of 3.2 mg/mi for 6 3-phase tests) than site 2 (an average of 2.6 mg/mi) for the Explorers, site 1 has less mass (2.4 mg/mi) than site 2 (2.8 mg/mi) for the Escorts.

Table IV.

Particulate and Manganese Emissions from Explorers						
Vehicle Number	Odometer (Miles)	Site 1 PM (mg/mi)	Site 2 PM (mg/mi)	Site 3 Mn (µg/mi)	Site 4 Mn (µg/mi)	Fraction of Mn Emitted
304	55,105 ^a	1.49 ^d ±1.11	3.09 ^f ±0.25	n.a.	135 ^f	7.9%
	55,182 ^a	7.25 ^d ±0.72	7.70 ^f ±0.31	116 ^d	115 ^f	6.8%
305	5,123 ^a	n.a.	0.08 ^c ±0.42	3 ^e		
	20,272 ^a	2.31 ^d ±0.68	1.28 ^e ±0.92	6 ^d	3 ^f	
	55,173 ^a	n.a.	2.13 ^f ±0.49	2 ^d	3 ^f	
	55,250 ^a	2.08 ^d ±1.03	2.18 ^f ±0.35	2 ^d	1 ^f	
	55,326 ^a	1.39 ^d ±2.09	2.50 ^f ±0.31	3 ^d	1 ^f	
306	5,141 ^a	n.a.	1.70 ^c ±0.32	173 ^e	181 ^e	10.4%
	20,213 ^a	3.59 ^d ±1.55	2.82 ^f ±0.44	186 ^f	158 ^h	10.1%
	20,290 ^a	3.73 ^d ±0.30	2.71 ^e ±0.62	122 ^d	132 ^f	7.5%
	55,273 ^a	3.97 ^d ±0.46	1.92 ^f ±0.40	325 ^d	289 ^f	18.1%
	55,349 ^a	5.79 ^d ±0.44	4.62 ^f ±0.58	227 ^d	232 ^f	13.5%
307	55,158 ^a	3.24 ^d ±0.93	4.63 ^f ±0.32	4 ^d	4 ^f	
	55,226 ^a	3.93 ^d ±0.62	3.62 ^f ±0.31	6 ^d	4 ^f	
^a Average of six - three phase tests ^b One three phase UDDS test ^c TX40 filter ^d Zeffluor filter 0.5 µ pore size ^e Zeffluor filter 1.0 µ pore size ^f PTFE filter 0.2 µ pore size ^g PTFE filter 0.45µ pore size ^h T60A20 filter						

Table V.

Particulate and Manganese Emissions from Escorts						
Vehicle Number	Odometer (Miles)	Site 1 PM (mg/mi)	Site 2 PM (mg/mi)	Site 3 Mn (μ g/mi)	Site 4 Mn (μ g/mi)	Fraction of Mn Emitted
315	5,108 ^a	0.11 ^f ±0.31	0.83 ^d ±0.38	1 ^f	0 ^d	
	20,029 ^a	n.a.	n.a.	4 ^d	3 ^f	
	20,187 ^a	2.75 ^e ±0.27	2.30 ^f ±0.47	10 ^d	8 ^f	
	20,264 ^b	3.92 ^e ±1.97	2.83 ^f ±1.50	10 ^d	10 ^f	
	55,100 ^a	1.71 ^d ±1.32	2.66 ^f ±0.33	3 ^d	2 ^f	
	55,177 ^a	1.52 ^d ±0.44	1.41 ^f ±0.43	1 ^d	2 ^f	
316	5,113 ^a	0.78 ^f ±0.34	2.93 ^d ±0.33	11 ^g	10 ^d	1.1%
	20,025 ^a	1.77 ^d ±0.30	1.72 ^f ±0.33	123 ^d	119 ^f	12.1%
	20,103 ^b	3.00 ^d ±1.35	4.89 ^f ±1.20	148 ^d	133 ^f	14.0%
	20,115 ^{b1}	-0.13 ^d ±1.17	3.17 ^f ±1.51	31 ^d	29 ^f	3.0%
	20,252 ^a	2.83 ^e ±0.47	1.91 ^f ±0.23	191 ^d	173 ^f	18.2%
	20,328 ^b	3.12 ^e ±2.02	2.60 ^f ±1.27	242 ^d	243 ^f	24.3%
	55,100 ^a	4.10 ^d ±0.45	4.80 ^f ±0.39	448 ^d	458 ^f	45.3%
	55,177 ^a	3.35 ^d ±0.43	4.59 ^g ±0.38	418 ^d	415 ^g	41.7%
317	55,114 ^a	1.60 ^d ±0.29	0.94 ^f ±0.36	2 ^d	4 ^f	
	55,191 ^a	3.37 ^d ±0.77	1.88 ^f ±0.29	2 ^d	n.a.	
^a Average of six - three phase tests ^b One - three phase UDDS test ^{b1} One highway fuel economy test ^c TX40 filter ^d Zeffluor filter 0.5 μ pore size ^e Zeffluor filter 1.0 μ pore size ^f PTFE filter 0.2 μ pore size ^g PTFE filter 0.45 μ pore size ^h T60A20 filter						

The total particulate mass emissions from the MMT-fueled vehicles are generally between 0 to 2.0 mg/mi higher than those from the MMT-free

vehicles. This difference is significant even with the 0.5 mg/mi variability in repeat particulate mass measurements (Table VI, Figures 1 and 2).

Table VI.

Effect of MMT on Total Particulate Emissions						
Odometer (miles)	Explorers			Escorts		
	MMT (mg/mi)	MMT-free (mg/mi)	Delta (mg/mi)	MMT (mg/mi)	MMT-free (mg/mi)	Delta (mg/mi)
5,000	1.7	0.08	1.6	1.9	0.5	1.4
20,000	3.2	1.8	1.4	2.1	2.5	-0.4
55,000	4.1	2.1	2.0	4.2	1.8	2.4

Particulate Mass Emissions
from Explorers

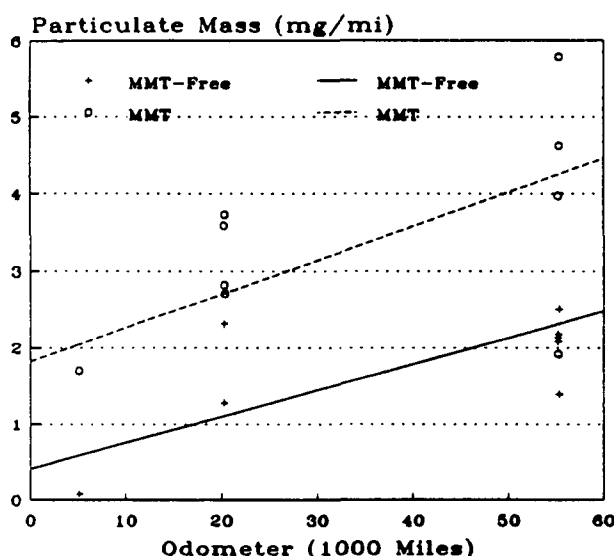


Figure 1

The manganese particulate emissions for the vehicles using MMT-free fuel are between 1 and 10 $\mu\text{g Mn/mile}$ (Tables IV and V) while that for the MMT vehicles are generally between 120 and 450 $\mu\text{g Mn/mile}$, or between 6% and 45% of the Mn combusted in the fuel. The Explorers get about 17 mpg so they combust about 1700 $\mu\text{g Mn/mi}$, and the Escorts get about 30 mpg so they combust about 1000 $\mu\text{g Mn/mi}$. Assuming the manganese is emitted as Mn_3O_4 (2), the 120 to 450 $\mu\text{g/mi}$ emissions of Mn corresponds to 0.17 to 0.63 mg/mi of particulate mass.

Particulate Mass Emissions
From Escorts

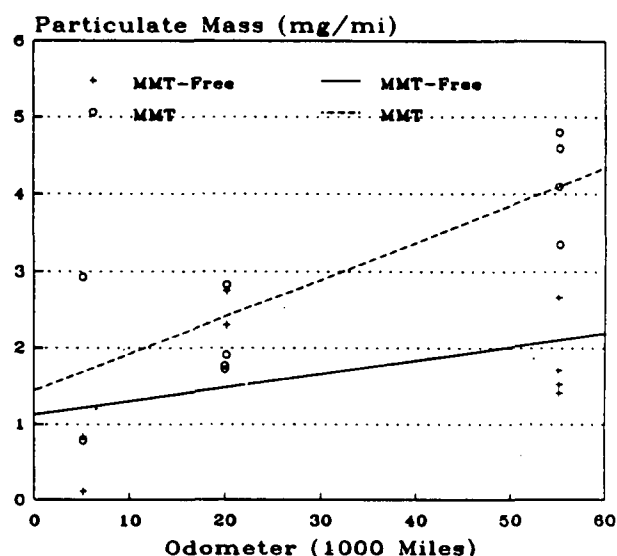


Figure 2

The Mn emissions from both the Escorts and Explorers increase with mileage accumulation, see Figures 3 and 4. The Mn emissions appear to increase steadily to 55,000 miles.

The manganese found in the engine oil from vehicles using MMT-free fuel ranges from 1 to 10 ppm by weight (Tables VII and VIII) while that for the MMT vehicles 100 to 325 ppm, or between 5% to 11% of the Mn combusted in the fuel. The wear elements, Cu, Pb and Fe, found in the oil do not appear to be correlated to the use of MMT.

Manganese Emissions from Explorer 306

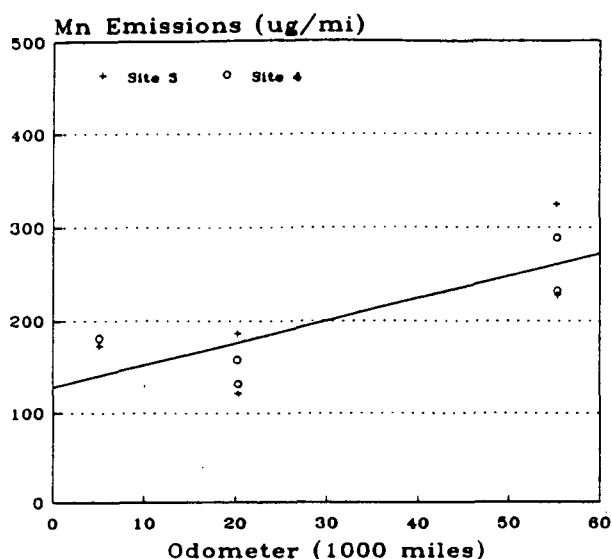


Figure 3

Manganese Emissions from Escort 316

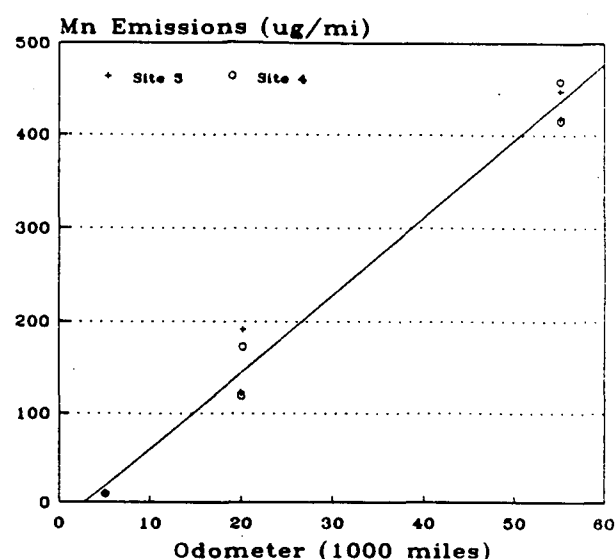


Figure 4

DISCUSSION

The effect of MMT on manganese and particulate emissions from four Escort and four Explorer vehicles has been studied on a chassis dynamometer. Two vehicles of each type used MMT fuel at 0.029 g Mn/gal; the remaining vehicles used Mn-free fuel. The Escort and Explorer fuel economies were 30 and 17 mpg, respectively. The vehicles accumulated mileage on public roads and were tested at 5K, 20K and 55K miles on the dynamometer.

During this testing, from 6% to 45% of the Mn used in the fuel was emitted as air-borne particulate matter. This generally agrees with earlier work which cites that about 20% of the Mn consumed is emitted as air-borne particles (3). In this work, both the particulate mass and the Mn emissions steadily increased with mileage accumulation, see Figures 1 to 4. The increasing Mn emissions may be due to an initial build up and subsequent stabilization of Mn deposits in the engines and exhaust systems.

Ethyl recently reported that only 0.4% of the fuel Mn was emitted (6). While the reason for their low Mn emissions is unknown, it may be due to low mileage accumulation. Indeed, the average Mn emitted by the MMT-free vehicles in this work was about 7 $\mu\text{g}/\text{mi}$ which is nearly the same as that reported for the MMT vehicles

reported by Ethyl (6) (Table IV and V).

According to the EPA, emission of 20% of the fuel manganese as air-borne particles may represent a health hazard (4) since manganese can be neurotoxic when inhaled in excessive amounts. They say exposure to more than 0.4 $\mu\text{g}/\text{m}^3$ of Mn for 24 hours per day over 70 years may cause symptoms. This concentration, called the "inhalation reference concentration," has about a ten-fold uncertainty factor (4). It ranges from 0.073 to 0.73 $\mu\text{g}/\text{m}^3$.

Assuming widespread use of MMT and using an approximate model, the EPA predicts that a typical office worker would be exposed to an average concentration of 0.05, 0.07 and 0.08 $\mu\text{g}/\text{m}^3$ of Mn if 10%, 20% and 30% of the MMT used in the vehicle fleet fuel was added to the ambient particulate matter, respectively (4). That is, a large fraction of the U.S. population would be exposed to Mn at, or above, the lower limit of inhalation reference concentration. They also predict that the most highly exposed 1 million people in the U.S. population would experience average concentrations of 0.16, 0.31 and 0.45 $\mu\text{g}/\text{m}^3$ of Mn if 10%, 20% and 30% of the MMT used in the vehicle fleet was added to the ambient particulate matter, respectively.

In this work, about 50% to 80% of the Mn used in the fuel was unaccounted for. In addition to the 10% to 45% emitted during dynamometer testing, about 8% was found in oil

drained from the engines. Some of the missing Mn may be stored in the engine, catalyst and exhaust systems which will be analyzed when

the vehicles reach 105,000 miles, and some may be emitted while driving on public roads.

Table VII.

Oil Analysis from Explorers							
Vehicle Number	Odometer (miles)	Mn Found (ppm)	As % Mn Expected (%)	Fe Found (ppm)	Cu Found (ppm)	Pb Found (ppm)	Si Found (ppm)
304	15,651	191	5.78%	17	18	17	26
	22,184	221	8.43%	20	15	16	31
	30,130	235	7.37%	16	59	14	16
	37,400	325	11.14%	21	29	22	14
	45,015	214	7.00%	14	47	19	10
	52,441	276	9.26%	17	27	25	11
	59,988	238	7.86%	15	74	24	9
	Average	243		17	42	20	14
305	12,748	0		17	17	19	17
	20,425	0		17	14	16	15
	27,621	10		12	26	16	7
	35,167	5		14	21	20	11
	42,482	1		14	54	20	7
	49,792	1		12	45	22	9
	57,244	1		17	58	23	6
	Average	3		15	34	19	10
306	12,470	158	5.47%	14	18	17	13
	20,565	270	8.31%	20	15	18	14
	27,585	257	9.12%	17	59	12	7
	35,184	218	7.15%	16	18	14	8
	42,485	194	6.62%	15	46	16	6
	49,950	320	10.68%	27	23	26	10
	Average	236		18	30	17	10
307	7,467	3		57	46	68	120
	15,811	1		21	30	21	36
	22,218	2		24	25	21	36
	29,957	2		12	23	19	17
	37,643	2		14	20	24	15
	45,230	1		13	18	21	12
	52,406	2		16	21	25	16
	Average	2		22	26	28	36

Table VIII.

Table VIII.

Oil Analysis for Escorts							
Vehicle Number	Odometer (miles)	Mn Found (ppm)	As % Mn Expected (%)	Fe Found (ppm)	Cu Found (ppm)	Pb Found (ppm)	Si Found (ppm)
315	12,236	4		26	32	30	64
	20,337	4		19	24	30	35
	27,526	1		15	19	26	20
	35,184						
	42,309	1		12	21	22	13
	49,878	2		14	29	31	13
	Average	2		17	25	28	29
316	12,241	126	6.36%	26	25	17	52
	20,401	196	8.45%	38	19	19	33
	27,628	177	8.61%	24	21	20	19
	34,828	197	9.62%	18	18	21	15
	42,638	177	7.97%	13	18	18	13
	49,987	195	9.33%	16	22	24	14
	Average	178		23	21	20	24
317	14,723	5		19	37	17	44
	22,135	3		17	24	19	29
	30,576	2		27	24	27	25
	37,446	1		28	23	25	17
	44,969	1		25	23	23	16
	52,056	1		21	28	28	17
	Average	2		22	27	23	26

During this testing, the total particulate emissions were roughly about 2 mg/mi for MMT-free fuel and 5 mg/mi for MMT fuel in approximate agreement with Ethyl's work (6) and earlier Ford data for Taurus vehicles using MMT-free fuel (7). These particulate emission rates are between 16 to 40 times lower than the 80 mg/mi standard in the 1990 Clean Air Standard and between 6 to 15 times lower than

the 30 mg/mi, emission rate for gasoline vehicles assumed by Adler and Cary (8) in their paper of air toxics emissions from motor vehicles.

Finally, emission rates at this level are difficult to measure accurately using one 3-phase test; most of the testing done here used 6 repeated 3-phase tests to collect sufficient particulate mass for accurate mass measurements (Tables III, IV and V).

APPENDIX

Table AI.

Gasoline Properties			
	Method	Durability Fuel	EEE Fuel
Gravity °API 60°F	ASTM D 1298	58.7	58.7
Research Octane	ASTM D 2699	91.4	96.6
Motor Octane	ASTM D 2700	83.1	87.6
Sensitivity		8.3	
(R + M)/2		87.25	92.1
Lead, g/gal	ASTM D3237	<0.002	<0.001
Sulfur, wt%	x-ray	0.029	0.0051
Phosphorus, g/gal	ASTM D 3231	<0.0008	0.0002
Manganese, g/gal	ASTM D3831-79	<0.001	
Reid Vapor Pressure, lb	ASTM D 323	9.2	9.2
Distillation, °F	ASTM D86		
10% Evap.		120	123
50% Evap.		198	222
90% Evap.		322	316
EP		404	401
Recovery, %		98.2	97.3
Residue, %		1.0	0.9
Loss, %		0.8	1.8
Acidity of Residue	ASTM D 1093	Pass	
Temp. for V/L 20, °F	ASTM D2533	135	
Hydrocarbons, vol. %	ASTM D 1319		
Aromatics		31.6	31.3
Olefins		1.4	1.7
Saturates		67.0	67.0
Benzene, vol. %	Chevron Refractive Index	1.23	

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The Effect on Emissions and Emission Component Durability by the Fuel Additive Methylcyclopentadienyl Manganese Tricarbonyl (MMT)

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ABSTRACT

Vehicle emissions have been measured and the results statistically evaluated for a vehicle test fleet consisting of four Escorts and four Explorers using both methylcyclopentadienyl manganese tricarbonyl (MMT) at 1/32 gram Mn/gallon and clear (MMT free) fuel. The fleet was divided in half -- half with MMT and half without MMT doped fuel. This interim report covers emission measurement results at 5,000; 15,000; and 50,000 miles of exposure to MMT doped fuel. The planned mileage accumulation is for 100,000 miles of durability and exposure to MMT based fuel. A modified paired t-test is used to analyze the emission data obtained from all the fleet vehicles. The statistical evaluation of both feedgas and tailpipe emissions indicated that the use of MMT is detrimental to emissions of HC at both the 15,000 mile and 50,000 mile levels of MMT exposure. Indications also are as mileage is accumulated, the worse the effect on HC by MMT. CO tailpipe emission responses at 15,000 miles show a deleterious effect by MMT but a beneficial effect at 50,000 miles. All NO_x emission responses show a beneficial effect by MMT at the 15,000 mile level but all emission responses indicate a deleterious effect at 50,000 miles by MMT. Particulate emissions are described in a companion report. The physical and chemical characterization, as well as the final emission results, of emission components will be reported following completion of the program at 100,000 miles.

Introduction

Section 211(f)(1) of the Clean Air Act prohibits the sale of fuels or fuel additives which are not "substantially similar" to a base unleaded gasoline. However, section 211(f)(4) allows the EPA Administrator to grant waivers of section 211(f)(1) if neither the fuel nor its emission products will "cause or contribute to a failure of any emission control device or system ... to achieve compliance by the vehicle with the (applicable) emission standards. Measurement of the regulated and the so called "non-regulated" emissions are required to show that gasoline additives do not cause emissions that could harm the environment. Specifically, a fuel additive could cause such damage directly by forming harmful combustion products or indirectly by damaging vehicle emission control systems. The combustion products of methylcyclopentadienyl manganese tricarbonyl (MMT), Mn_3O_4 , is known to accumulate in engines¹, on exhaust catalysts² and to be released into the atmosphere. In each instance, it has the potential to harm the environment. In the engine, it can cause increased regulated emissions¹, especially of hydrocarbons. On catalysts, it may cause premature deactivation by coating with a layer of impenetrable Mn_3O_4 or clogging the inlet to the catalysts.⁴

Methylcyclopentadienyl manganese tricarbonyl (MMT), commercially labeled by Ethyl Corporation as HITEC 3000, is used as an octane enhancer. In September, 1978 the addition of MMT to gasoline fuel in the U. S. was denied by the EPA. This denial was based on the failure of Ethyl Corporation to establish that the additive MMT would not cause or contribute to the failure of any 1975 or later model year vehicle to comply with applicable emission standards. Although banned in the U. S., MMT has been used in Canadian leaded and unleaded gasolines at a concentration level of 1/16 gram Mn/gallon for over 10 years. During that time Ethyl claims that they have had no emission component or environmental related problems due to MMT in Canada. Since Ethyl's first waiver submission in 1978 they have submitted waiver requests to the EPA twice more at different concentration levels, each time being refused because of lack of supporting data. The third request in May, 1990 for a concentration level of 1/32 gram Mn/gallon followed extensive vehicle testing by Ethyl. Ethyl's vehicle test results show a decrease in NO_x and CO but a small significant increase in HC emissions with vehicles fueled with MMT doped fuel. Ethyl withdrew its third waiver request, October, 1990, five days prior to the end of the statutory 180-day review period citing differences with the EPA as to the amount of particulate being emitted from test vehicles.

All earlier vehicle and laboratory tests at Ford and other automotive companies (1978 - 1982) have shown degradation of HC emissions without improvement in either of CO and NO_x . However, these tests were at a concentration level greater than that of the current waiver. Our most recent experience has also been with a greater MMT concentration level (1/16 gram Mn/gallon). This experience included physical and chemical characterization of both warranty and non-warranty in-use Canadian catalysts. Our results in these studies did not support Ethyl's contention that MMT would not deter emission component effectiveness, especially the catalyst. To the contrary, our studies show significant deterioration of emission components when exposed to the MMT based fuel. Unfortunately, few, if any, U. S. automaker has had vehicle emission or catalyst characterization data at the proposed waiver's 1/32 gram

Mn/gallon concentration level. Thus, evaluations of the effects of MMT on emission components were projected from the higher concentration levels used in Canada.

The acceptability of MMT as a U.S. gasoline additive depends upon the magnitude of the effects on emission components, engine, and the release into the atmosphere. The magnitude, in turn depends on the level of MMT added to the gasoline and used by U. S. customers. The objective of the current vehicle fleet and subsequent laboratory tests is directed at obtaining actual vehicle emission and emission component characterization data at the concentration level of 1/32 gram Mn per gallon using a fully formulated fuel.

Vehicle Description

Eight vehicles (Table 1) were selected for this comprehensive study, four 4.0L Explorers and four 1.9L Escorts (CT-20). The Escorts were 1991 production vehicles equipped with a manual transmission, sequential electronic fuel injection and one close mounted 92 in³ three way catalyst (Pd:Rh, 9:1, 60 g/ft³ precious metal loading). The Explorers were also 1991 production vehicles with the exception that each was equipped with a 1993 production prototype engine. This set of vehicles was being tested concurrently for 100,000 mile engine component durability. The MMT fuel study with the Explorers was an add-on study to the engine durability study. The Explorers were equipped with automatic transmissions, sequential electronic fuel injection and 2 underbody 75 in³ three way catalysts (Pt:Rh, 5:1, 40 g/ft³ precious metal loading). These vehicles were also equipped with two oxygen sensors for each side of the engine exhaust. During the test sequence both the Escorts and Explorers underwent routine owner manual checks.

TABLE 1

MMT Fleet Test Vehicles			
Vehicle	Test Number ¹	Engine Size	Test Fuel ²
Explorer	304	4.0	Clear + MMT
Explorer	307	4.0	Clear
Explorer	305	4.0	Clear
Explorer	306	4.0	Clear + MMT
Escort	315	1.9	Clear
Escort	316	1.9	Clear + MMT
Escort	317	1.9	Clear
Escort	318 ³	1.9	Clear + MMT

Note 1: Vehicles were paired, 304-307, 305-306, 315-316, 317-318.

Note 2: Clear Fuel was Chevron durability fuel, Clear fuel + MMT containing 1/32 gram Mn/gallon as MMT.

Note 3: Escort 318 was involved in a vehicular accident at 8,000 miles into the test. This accident necessitated the removal of the engine and emission components and replacing them at 10,117 miles with new hardware. Following a similar 5,000 miles break-in period with clear Chevron fuel, the vehicle returned to mileage accumulation with Clear + MMT fuel.

Durability Test Fuel

The base fuel used for this durability study was Chevron UL/CQ Unleaded Gasoline. This fuel contains Chevron's patented Techroline (Polyether Amine Gasoline Additive) gasoline additive in the concentration commercially available in Chevron Unleaded Gasoline. This fuel was selected as a durability fuel because it contained detergent additives that would normally be encountered in customer driving. Table 2 lists the durability fuel analysis as supplied by Chevron (CRR-6366). The MMT additive was blended in 1000 gallon batches to the Chevron fuel to match the 1/32 (0.0313) grams Mn/gallon standard being proposed by Ethyl. The properties of MMT have been adequately described in a recent SAE paper¹. The fuel was stored in 1000 gallon tanks for access by the fleet. Chemical analysis of the MMT doped fuel was taken after each filling of the storage tank to insure the correct MMT concentration. The average MMT concentration used by the fleet was 0.0289 ± 0.0025 grams Mn/gallon. Two vehicles from each class were run on the Chevron durability fuel without the MMT fuel additive and two with the Chevron durability fuel with the MMT additive.

Durability Test Cycle

The driving test cycle selected for this study is summarized as follows:

- 5% city driving,
- 5% gravel or off road driving,
- 20% rural driving, and
- 70% highway driving.

This drive test cycle is representative of normal customer driving.

The vehicles were driven at an average speed of 54 MPH and approximately 415 miles per shift. Specifically, the drive cycle is summarized below.

- City schedule was run south of Grand Blanc. Speed limits range from 25 to 45 MPH.
- Gravel schedule was run south of Grand Blanc. Speed limits range from 25 to 45 MPH.
- Rural schedule as run east and west of Grand Blanc on paved 2 lane roads. Speed limits range from 45 to 55 MPH.
- Highway schedule was run between Flint and Port Huron on I-69. Speed limit is 65 MPH.
- City, gravel and rural schedules are within a 25 mile radius of Grand Blanc. Drivers were instructed to follow posted speed limits.

TABLE 2

CHEVRON UNLEADED GASOLINE PROVIDED AUTO
MANUFACTURERS FOR EMISSIONS DURABILITY TESTS

Tank No.		308
Batch No.		44
Gravity, °API at 60° F (15.6° C)	ASTM D 1298	58.7
Research Octane Number	ASTM D 2699	91.4
Motor Octane Number	ASTM D 2700	83.1
Sensitivity		8.3
(R+M)/2		87.25
Lead, g/Gal.	ASTM D 3237	< 0.002
Sulfur, Wt %	X-Ray	0.029
	ASTM D 2622 (Modified)	
Phosphorus, g/Gal.	ASTM D 3231	< 0.0008
Manganese, g/Gal.	ASTM D 3631-79	< 0.001
Gum, mg/100 ml	ASTM D 381	
Unwashed		3.5 ¹
Washed		1
Reid Vapor Pressure, Lb	ASTM D 323	9.2
Distillation, °F (°C)		
(% Evaporated)	ASTM D 88	
10%		120 (49)
50%		198 (92)
90%		322 (161)
EP		404 (207)
Recovery, %		98.2
Residue, %		1.0
Loss, %		0.8
Acidity of Residue	ASTM D 1093	Pass
Temp. for V/L 20, °F (°C)	ASTM D 2533	135 (57)
Hydrocarbons, Vol. %	ASTM D 1318	
Aromatics		31.8
Olefine		1.4
Saturates		67.0
Benzene, Vol. %	Chevron Research Technique	1.23
Water and Sediment, Vol. %	ASTM D 2708	0.00
Oxidation Stability, Hr	ASTM D 525	>24
Copper Corrosion	ASTM D 130	1

¹ Prior to addition of Techroline deposit control additive.

Emission Tests

The eight vehicles being used for this comprehensive study are planned to accumulate 100,000 miles of durability with and without MMT based fuel. To establish a baseline, all test vehicles accumulated the first 5,000 miles on the test durability fuel containing no MMT additive. In order to statistically determine the effect of MMT on emissions, six baseline tests were then conducted on all vehicles. Following the first 5,000 miles, two of each class of vehicles began to accumulate mileage with MMT doped fuel (1/32 g Mn/ gallon). The remaining two Escorts and two Explorers continued to accumulate mileage on the durability fuel without MMT. This sequence of testing is summarized in Table 3.

TABLE 3

Emission Test Sequence

Program Miles	Number of Tests at Listed Mileage Intervals					
	-	0	15	50	80	100
Actual Odometer Miles	0	5	20	55	85	105
Explorer #305 & #307	-	6	6	6	note 2	6
Explorer #304 & #306	-	6	6	6	note 2	6
Escort #315 & #317	Note 1	6	6	6	note 2	6
Escort #316 & #318	Note 1	6	6	6	note 2	6

Note 1: The Escorts were at 4K under a separate test program, an additional 1000 miles of aging with durability fuel was accumulated prior to baseline testing.

Note 2: Two of the Explorers, #'s 305 and 307 were in addition tested at 55,000 and 85,000 miles emissions tested as part the shared durability program with engine for spark plug durability. The remaining two Explorers, #'s 304 and 306 had duplicate emission tests at 85,000 only two emission tests were performed on vehicles not involved in durability testing.

All emission tests were performed with "Indolene Clear" certification fuel (without MMT). The selection of "Indolene Clear" certification fuel for emission testing was to insure that the emissions obtained would be the result of emission components deterioration and not the fuel. The standard emission tests (CVS-C/H excluding Heat Build and Evaporative Tests) were performed on one cell (Chassis Cell #2) at the Ford Certification Test Laboratory. This procedure was selected to eliminate cell to cell variability. Particulate testing was performed at the Scientific Research Laboratory's Chassis Rolls using the Chevron durability fuel with and without MMT. These tests and results will be described in detail in companion report³.

Experimental Design, Data Collection and Analysis

A modified paired t-test was used to analyze the emission data obtained from the paired fleet vehicles. In each case two similar vehicles were randomly selected to be a pair. During initial aging (5000 miles to establish baseline), both vehicles were operated on clear fuel (Chevron Durability fuel without MMT). After the initial aging period one of the two vehicles was randomly selected to operate on the MMT treated Chevron durability fuel; the other vehicle in the pair remained on the clear Chevron durability fuel.

At the end of the initial aging period (5000 miles), six replicate cold/hot tests (standard FTP) were performed on each vehicle in the pair. The difference in the mean values provided the expected difference between the vehicle pairs, $E(\bar{d})$. The vehicles then operated on their respective fuels, tested again at 20,000 miles (odometer). The difference in the mean values at this point represented the difference due only to MMT (\bar{d}). This was again repeated at 55,000 miles (odometer), with the mean difference at this point providing another difference due only to MMT.

The t-statistic was used to evaluate the significance of the MMT effect. Based on an $H_0: \bar{d} = 0$ (no effect by MMT) and an $H_a: \bar{d} \neq 0$ (there is an effect of MMT), the following function called t_{calc} was calculated.

$$t_{calc} = \frac{\bar{d} - E(\bar{d})}{\frac{s}{\sqrt{n}}} \quad (1)$$

where "s" is a pooled estimate of test error, and "n" is the total number of observations. The value of " t_{calc} " was compared to tabled t_{crit} values to allow a decision on significance at the 95% confidence interval (two-sided test, α).

Each vehicle was tested (replicated) six (6) times at each mileage point to provide the design level accuracy of the differences due to MMT. Caution was used to avoid plot errors between each vehicle pair at each mileage point, by having both vehicles tested at or about the same time (this was accomplished early in the test program but as the mileage increased above 55,000 miles (odometer) the time to accumulate mileage varied a little more than earlier in the program due to vehicle maintenance problems). These data will be extended to 105,000 miles (odometer) as the mileage accumulation is completed.

Results and Discussion

All responses were evaluated using the same technique described above. Responses included all emissions (HC, CO, NO_x) by total and by bag, for both feed gas and tailpipe emission numbers. The vehicles tested included two pairs of each of two of the two vehicle make and models. The statistical results for feed gas analysis based on all vehicles combined are shown in figures 1-3. The numerical representation of these results are shown in the appendix (tables 5-7). Graphically, in each figure a positive number represents a statistically detrimental effect on emissions by the fuel additive MMT and a negative number represents a statistically beneficial effect. The middle bar represent the mean and the upper and lower bars represent the 95% confidence interval values.

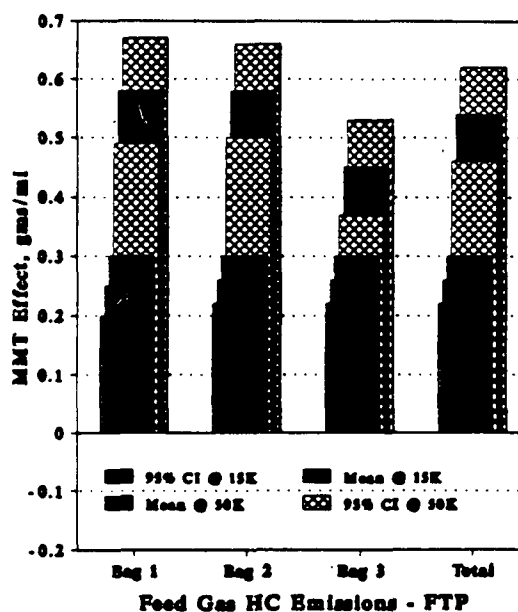


Figure 1

Feed Gas - As shown in figure 1 the results indicate that at both the 15,000 and 50,000 mile interval there is a significant detrimental effect of MMT on the HC feed gas emissions; the higher the mileage, the

greater the detrimental effect. Feed gas emissions for CO, figure 2, are somewhat mixed depending on bag number or total. The NO_x emissions, Figure 3, show that at 50,000 miles MMT affects the NO_x feed gas emission detrimentally although at 15,000 miles, the effect is beneficial. Although the data shown in Figures 1-3 represent the statistical analysis of the results for all the test vehicles combined, individual pairs exhibit about the same characteristic MMT directional effects; magnitude, by model and make, differs considerably.

Tailpipe - Tail pipe emissions are graphically shown for all vehicles in Figures 4-6. These results show that tailpipe HC emissions are detrimentally affected by MMT at both 15,000 and 50,000 miles. Again as mileage is accumulated, the magnitude of the effect grows. CO is detrimentally affected at 15,000 but shows beneficial effects at 50,000 miles. NO_x bag data show somewhat mixed results; only bag 3 shows a beneficial effect at both 15000 and 50000 miles. Except for bag 3, all other responses are affected detrimentally by MMT at both 15,000 and 50,000 miles.

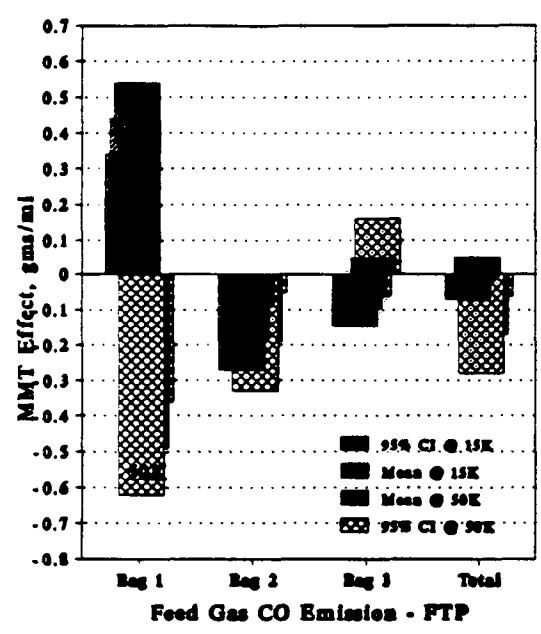


Figure 2

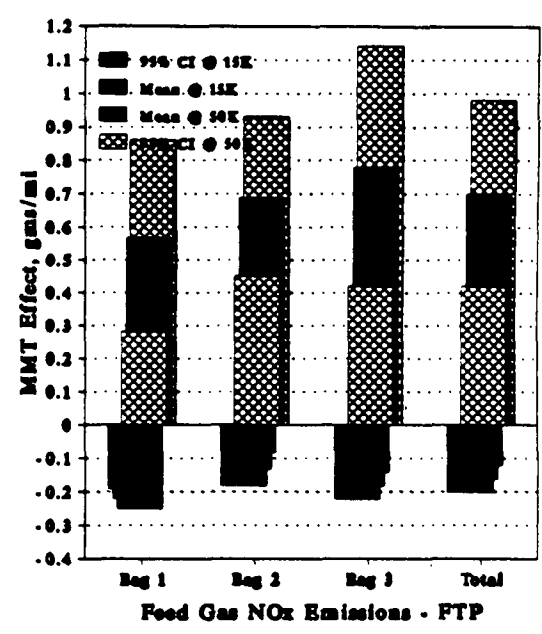


Figure 3

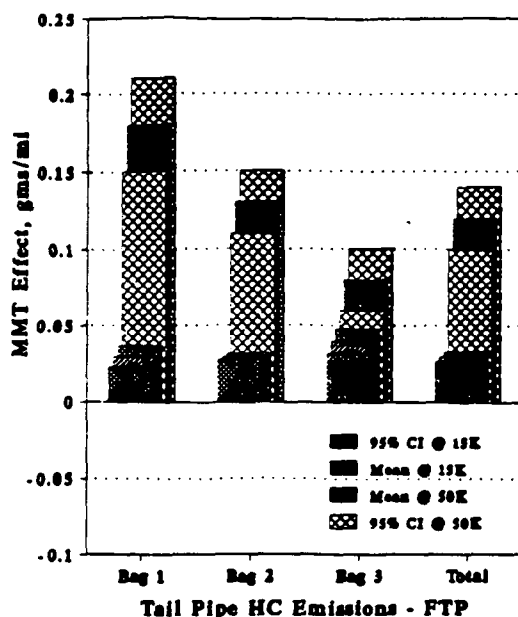


Figure 4

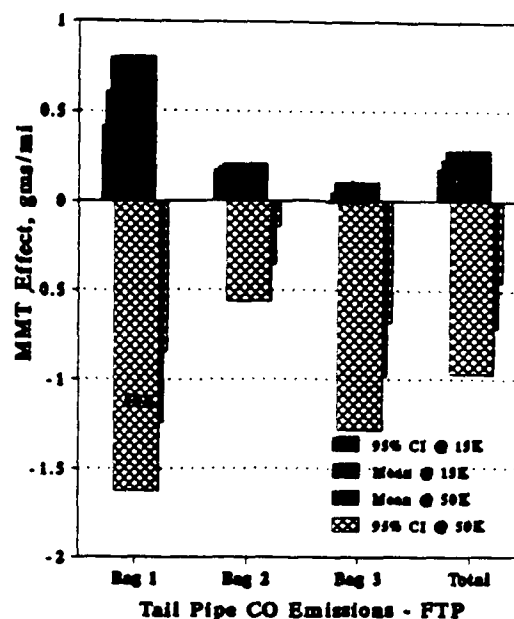


Figure 5

Summary (Emissions to 50,000 miles)

The results summarized in Table 4 are over the 4 pairs of vehicles, Explorers and Escorts, that were used in the fleet tests. In general, at the 95% confidence level for:

HC: All emission responses both feedgas and tailpipe indicate a harmful or detrimental effect by MMT at both the 15,000 and 50,000 miles levels of exposure by MMT. Results show that as mileage is accumulated, the worse the effect of MMT. Based on the current HC emission standard of 0.41 gms/mile this represents a 30% increase in HC emissions. Projecting this increase to the ULEV standard of 0.040 gms/mile this represents a 300% increase in HC emissions.

- CO:**
- (1) All emission responses at 50,000 miles indicate a beneficial effect of MMT, except for bag 3, feed gas.
 - (2) All feed gas responses at 15,000 miles indicate a beneficial effect of MMT, except for bag 1.
 - (3) All tailpipe responses including total, except bag 3 at 15,000 miles indicate a deleterious effect of MMT.

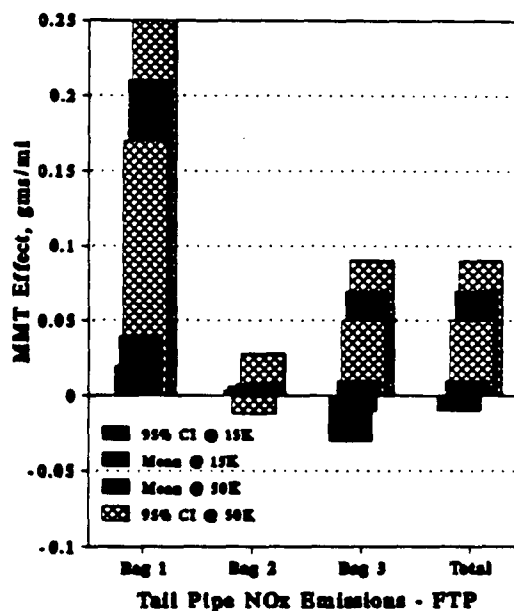


Figure 6

Statements (2) and (3) indicate a response type by mileage interaction. Mileage accumulation appears to improve the effect of MMT. Consequently, overall tailpipe responses represent a 21% decrease in CO emissions based on current CO standard of 3.4 gms/mile and a 41% decrease in CO emissions based on the 1.7 gms/mile ULEV standard for CO.

- NO_x: (1) All emission responses at the 50,000 mile level indicate a deleterious effect of MMT on emissions, except for bag 2, tailpipe.
- (2) All emission responses at the 15,000 mile level indicate a beneficial effect of MMT, except for tailpipe bags 2 and 3, and total tailpipe.

Statements (1) and (2) indicate a mileage by response type effect of MMT. Initially MMT has a beneficial effect, but at 50,000 miles the MMT effect is detrimental to emissions. Consequently, overall tailpipe responses represent an increase in NO_x emissions of 17% based on the current standard for NO_x 0.4 gms/mile and an increase of 35% based on the ULEV standard of 0.2 gms/mile.

TABLE 4

Summary of Statistical Evaluation of the Effect of MMT on Emissions

Pollutant	Feedgas (FG)			Tailpipe (TP)			Total	
MMT Miles	Bag 1	Bag 2	Bag 3	Bag 1	Bag 2	Bag 3	Feedgas	Tailpipe
HC	15 K	--	--	--	--	--	--	--
	50 K	--	--	--	--	--	--	--
CO	15 K	--	++	++	--	??	??	--
	50 K	++	++	??	++	++	++	++
NO _x	15 K	++	++	++	??	??	++	??
	50 K	--	--	--	??	--	--	--

Where "--" indicates that the effect of MMT is significantly detrimental
 "++" indicates that the effect of MMT is beneficial
 "??" indicates that the effect of MMT is inconclusive

In terms of the individual pairs (Escorts and Explorers), the detrimental effect of MMT on HC emissions generally agrees with that summarized above. CO shows some differences, and direction is unclear. The Explorers generally dictated and followed the "all" vehicle pairs results, basically due to the much larger effects shown by them. The Escorts due to a much smaller effect of MMT, showed the opposite effect of the Explorers; i.e. as mileage accumulated, the effect of MMT becomes more detrimental than that at 15,000 miles. The NO_x emissions results again follow the Explorers due to their larger effects; a strong mileage effect is shown (the more miles with MMT, the worse is the effect on emissions). The Escorts generally show a deleterious effect of MMT at both mileage points with little or no mileage effect, i.e., magnitude of the effect is independent of miles accumulated.

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APPENDIX

MMT EFFECT ON HC BY VEHICLE PAIRS

TABLE 5

HC		FG			TP			TOTAL	
		<u>1</u>	<u>2</u>	<u>3</u>	<u>1</u>	<u>2</u>	<u>3</u>	<u>FG</u>	<u>TP</u>
	<u>15K</u>								
	305/306	.43	.29	.25	.05	.02	.04	.31	.03
	304/307	.42	.36	.45	.05	.03	.09	.4	.05
	315/316	-.02	.01	.05	-.02	.04	.01	.01	.02
	317/316	.16	.38	.28	.02	.04	.01	.31	.03
	AVERAGE	.25	.26	.26	.03	.03	.04	.26	.03
	95% CI	±.049	±.04	±.04	±.007	±.002	±.008	.04	.003
<hr/>									
	<u>50K</u>								
	305/306	1.04	.96	.77	0.01	.01	-.03	.92	-.01
	304/307	.78	.73	.72	.2	.17	.13	.74	.17
	315/316	.14	.19	.05	.25	.16	.16	.14	.15
	317/316	.37	.42	.25	.26	.18	.07	.36	.17
	AVERAGE	.58	.58	.45	.18	.13	.08	.54	0.12
	95% CI	±.09	±.08	±.08	±.03	±.02	±.02	.08	.02

MMT EFFECT ON CO BY VEHICLE PAIRS

TABLE 6

CO		FG			TP			TOTAL	
		1	2	3	1	2	3	FG	TP
	<u>15K</u>								
	305/306	.75	-.02	.03	-.11	.2	-.01	.18	.08
	304/307	.65	-.7	.1	1.65	.13	.39	.21	.51
	315/316	-.23	-.27	-.38	-.02	.28	-.21	-.25	.08
	317/316	.61	.28	-.13	.91	.13	.01	.24	.23
	AVERAGE	.44	-.18	.095	.61	.19	.045	-.01	.23
	95% CI	±.10	±.09	±.05	±.19	±.016	±.056	±.06	±.05
.....									
	<u>50K</u>								
	305/306	-.93	-.62	-.64	-3.2	-.91	-2.54	-.66	-1.83
	304/307	-.97	-.81	.37	-2.16	-1.35	-1.64	-.53	-1.6
	315/316	-.36	.2	.12	-.05	0.36	-.04	.1	.16
	317/316	.29	.48	.36	.51	.49	.32	.41	.45
	AVERAGE	-.49	-.19	.05	-1.23	-0.35	-.98	-.17	-.71
	95% CI	±.13	±.14	±.11	±.39	±.21	±.30	±.11	±.26

MMT EFFECT ON NOx BY VEHICLE PAIRS

TABLE 7

		FG			TP			TOTAL	
		<u>1</u>	<u>2</u>	<u>3</u>	<u>1</u>	<u>2</u>	<u>3</u>	<u>FG</u>	<u>TP</u>
NOx	<u>15K</u>								
	305/306	-.32	.1	-.26	-.04	-.02	-.12	-.09	-.05
	304/307	-.32	-.4	-.37	-.05	.01	.02	-.38	-.01
	315/316	-.18	-.21	-.09	.08	.01	.01	-.17	.03
	317/316	-.05	-.01	.02	.09	.01	.04	-.01	.03
	AVERAGE	-.22	-.13	-.18	.02	.003	-.01	-.16	.0
	95% CI	±.03	±.05	±.04	±.02	±.003	±.02	±.04	±.009
	<u>50K</u>								
	305/306	-.35	.21	-.41	.33	.14	.20	-.07	.2
	304/307	2.53	2.27	3.19	-.05	-.04	-.04	2.58	-.04
	315/316	-.09	.02	0.1	.32	-.04	0.03	.02	.05
	317/316	.19	.78	.24	.24	-.03	.09	.25	.06
	AVERAGE	.57	.69	.78	.21	.008	.07	.70	.07
	95% CI	±.29	±.24	±.36	±.04	±.02	±.02	±.28	±.02